

Novel multiphase electrode/electrolyte composites for next generation of flexible polymeric Li-ion cells

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Abstract An innovative multiphase electrode/electrolyte composite is proposed here, which is obtained by a fast, versatile and easily scalable UV-induced free-radical photo-polymerisation technique. This novel configuration consists of a methacrylic-based polymer electrolyte directly formed in situ at the interface of different electrode films (i.e. commercial graphite and hydrothermally synthesized LiFePO_4). Conformal coatings are confirmed by SEM analysis which indicates an intimate interfacial adhesion between the electrode material particles and the polymer electrolyte. Laboratory-scale lithium pouch cells assembled by contacting a lithium metal counter electrode over the as-prepared electrode/electrolyte composites display good ambient temperature charge/discharge characteristics, at the level of the corresponding lithium cells in liquid electrolyte, along with very stable cyclability even at high current rates. In addition, preliminary results of a laboratory-scale Li-ion polymer cell, assembled by contacting the LiFePO_4 cathode with the graphite anode, both in situ coated with the polymer electrolyte, are presented. The obtained findings outline the practical relevance of the novel procedure adopted which leads to the preparation of composite films with interesting performance, particularly

for the next generation of flexible all-solid-state Li-ion microbatteries.

Keywords Electrode electrolyte composite · In situ photo-polymerisation · Polymer electrolyte · LiFePO_4 · Graphite · Lithium polymer cell

1 Introduction

Considering the environmental impact of the present transportation technologies relying on the consumption of fossil fuels, much attention has been given in the last decade to the so-called zero emission vehicles, i.e. the electric vehicle (EV) [1, 2]. Everyone agrees that the weak link in the technology is the battery and, clearly, without major improvements in the present technology, EVs will not gain widespread acceptance [3, 4]. Also, using better batteries, the emissions from hybrid electric vehicles can be reduced as they become less reliant on the combustion engine for propulsion.

As a consequence, in the near term, we expect a push for all-solid state, flexible, thin-film batteries to perform better and to undergo a rapid and substantial improvement [5]. Simultaneously achieving high energy density (i.e. material storage) and high power density (i.e. ion transport, rate capability) necessarily requires a high electrode/electrolyte interfacial area coupled with short diffusion distances within the electrodes themselves. Ultimately, if scientific discoveries prove to be scalable, cost-effective and easy to process, we should witness the large-scale reciprocation of EVs. This would also greatly influence emerging micro-scale technologies for the production of advanced small-scale flexible power system devices having potential applications in bendable polymeric electronics/

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microelectronics [6, 7], printed circuit boards, optics and sensors [8] and, particularly, aerospace systems [9] where they are being extensively considered to fit the hollow spaces of the future chassis. In this respect, the need of a low cost, green, safe and up-scalable production process becomes fundamental for the sustainable mass production of the next generation energy storage systems.

In this respect, the secondary lithium polymer batteries (LiPos) offer many advantages over traditional types of rechargeable power sources [10, 11]. LiPos have over 20 % higher energy density than Li-ions. They are physically different as they are assembled in flexible foil-like packages instead of rigid metal cases. This greatly reduces the weight and also allows for a variety of different form factors. The basic requirement for the development of lithium-based polymer batteries is the replacement of the commonly used liquid electrolyte with a polymer electrolyte which, ideally, would have the ionic conductivity of a liquid at ambient and/or sub ambient temperatures and the mechanical properties of a solid [4, 10, 11]. Such a material would serve both as the electrolyte and the separator, and it endows the battery with mechanical flexibility, a property unattainable in cells with conventional liquid electrolytes.

Nevertheless, this replacement is not a straightforward operation: the challenging requirement for the success is to achieve good compatibility between the main components: the electrodes and the electrolyte. The major problem is to assure a full wettability throughout the entire electrode bulk, a process which is naturally achieved when the electrode is immersed into a liquid solution but which must be activated or somewhat promoted when the same electrolyte is confined within a polymer matrix. Moreover, mastering the chemical stability of any new electrode material with respect to its operating polymer electrolyte medium, which requires a control over the electrode–electrolyte interface, is as important as designing new materials [12].

Generally, thin-film type batteries are fabricated using sequential deposition of current collectors, electrode active materials and solid/quasi-solid electrolytes by various deposition processes. Simplification of the fabrication process would expedite practical application and reduce manufacturing costs. One of the most effective methods for simplifying fabrication process would be to use in situ prepared materials. To this purpose, due to the versatile nature of the UV-induced free-radical photo-polymerisation technique, novel multiphase electrode/electrolyte composites are proposed here, in which a methacrylic-based quasi-solid polymer electrolyte is directly formed in situ at the interface with the electrodes (i.e. a hydrothermally synthesized LiFePO_4 lithium iron phosphate cathode and a commercial graphite anode), and their characteristics are fully described. From the perspective of

more effective battery design, improving performance revolves around raising the fraction of the electrochemically active components (namely, the electrodes) to as close to unity as possible, while decreasing the fraction of the supporting components (e.g. electrolyte, current collectors and packaging) to as near zero as possible. Regarding this last point, reducing the thickness of the electrolyte and eliminating the need for binders and conductivity additives are desirable strategies. Materials research has an important role to play in attaining these goals. The proposed approach would also overcome the kinetic limitations due to the ionic exchange between the electrode and the otherwise glassy surface of most of the polymer-based electrolyte membrane. The promising perspectives of such kind of novel electrode/electrolyte composites are illustrated by the experimental data regarding their electrochemical responses in laboratory-scale lithium-based polymer cells.

2 Experimental

2.1 Materials

The reactive formulation for the preparation of the polymer electrolyte comprised:

- bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA, Aldrich), a methacrylic-based di-functional oligomer having an average molecular weight of 1,700;
- poly(ethylene glycol) methyl ether methacrylate (PEGMA-475, average M_n : 475, Aldrich), the reactive diluent which can control the cross-linking density during the polymerisation reaction [13];
- bis(trifluoromethane)sulfonimide lithium salt (LiTFSI , $\text{CF}_3\text{SO}_2\text{N}(\text{LiSO}_2\text{CF}_3)$, battery grade), obtained from Ferro Corp. (USA), the source of Li^+ ions, dissolved in a mixed ethylene carbonate/diethyl carbonate (EC/DEC, Ferro Corp., battery grade) solution;
- 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173), provided by Ciba Specialty Chemicals, the free-radical photo-initiator.

The quick and low cost surfactant-assisted mild hydrothermal process developed by our Research Group [14] was used to prepare the nanostructured LiFePO_4 cathode material. The graphite anode material was obtained in the form of synthetic powder (particle size $< 20 \mu\text{m}$) from Aldrich. The high-purity lithium metal foils with a thickness of $125 \mu\text{m}$ were obtained from Chemetall (Frankfurt, Germany).

Before their use, BEMA and PEGMA-475 were kept open in the inert atmosphere of an Ar-filled dry glove box (Jacomex GP-II-S, O_2 and H_2O content $< 0.1 \text{ ppm}$) for

several days and also treated with molecular sieves (Molecular sieves, beads 4 Å, 8–12 mesh, Aldrich) to ensure the complete removal of traces of water/moisture from the liquid monomers.

2.2 Preparation of the multiphase electrode/electrolyte composites

The preparation procedure of the multiphase electrode/electrolyte composites is schematically illustrated in Fig. 1. First of all, the electrode (thickness of about 50 µm) was prepared by spreading a paste of the different components (i.e. active material, electronic conducting additive and binder) mixed in *N*-methyl-2-pyrrolidone (NMP, Aldrich) on a current collector (treated Al and Cu metal foils for the positive and the negative electrodes, respectively), by the so-called “doctor blade” technique. Particularly, LiFePO_4 powder was the cathodic active material, graphite the anodic active material, acetylene black the electronic conducting additive (Shawinigan Black AB50, Chevron Corp., USA) and poly(vinylidene fluoride) the binder (PVdF, Solvay Solef 6020). The positive electrode composition was 82:10:8 w/w with respect to LiFePO_4 :AB50:PVdF, while the negative electrode composition was 87:5:8 w/w with respect to graphite:AB50:PVdF. After the evaporation of the solvent by a mild heating at around 50 °C, the electrode films were hot pressed at about 120 °C and, successively, dried at 130 °C under high vacuum for 5 h.

The prepared electrode films were used as supporting substrate for the following in situ polymerisation step. The first step in the UV-induced one-shot photo-polymerisation process was the preparation of an appropriate liquid reactive mixture using the necessary ingredients such as polymer precursors (BEMA and PEGMA-475), lithium salt (LiTFSI) dissolved into an organic solvents (EC/DEC)

mixture and a radical photo-initiator (Darocur). The exact weight ratio of BEMA:PEGMA:EC/DEC:LiTFSI was 35:15:35:15 with the addition of 3 wt% of photo-initiator. This reactive mixture is an electrolyte itself as it has lithium salt dissolved inside. The polymer electrolyte precursor was drawn onto the electrode material film [14] and given enough time to wet the active material completely. Later, a calibrated wire-wound applicator was rolled over the substrate to obtain a final thickness over the substrate ranging from 70 to 100 µm. Thus, the overall thickness of the complete multiphase electrode/electrolyte composite was around 120–150 µm. The coated sheets were covered into UV transparent quartz boxes fluxed with nitrogen and this set up was then exposed to UV-irradiation for approx. 3 min. The photochemical curing was performed using a medium vapour pressure Hg UV lamp (Helios Italquartz, Milan, Italy), with a radiation intensity on the surface of the samples of about 30 mW cm⁻². These conditions assured quantitative conversion of the double bonds (disappearance of the allyl signal, checked by FT-IR).

All the procedures were carried out in an environmentally controlled dry room (10 m², R.H. < 2 % ± 1 at 20 °C) produced by SOIMAR (Caluso, Italy).

2.3 Analyses and characterisation techniques

The characterisation of the UV-cured polymer films and multiphase composites included real-time Fourier-transform infrared spectroscopy, thermogravimetric analysis and differential scanning calorimetry, scanning electron microscopy, electrochemical impedance spectroscopy and linear sweep voltammetry.

The kinetics of the photo-polymerisation process was investigated using FT-IR spectroscopy (NICOLET-5700 FT-IR instrument by Thermo Fisher Scientific Inc.,

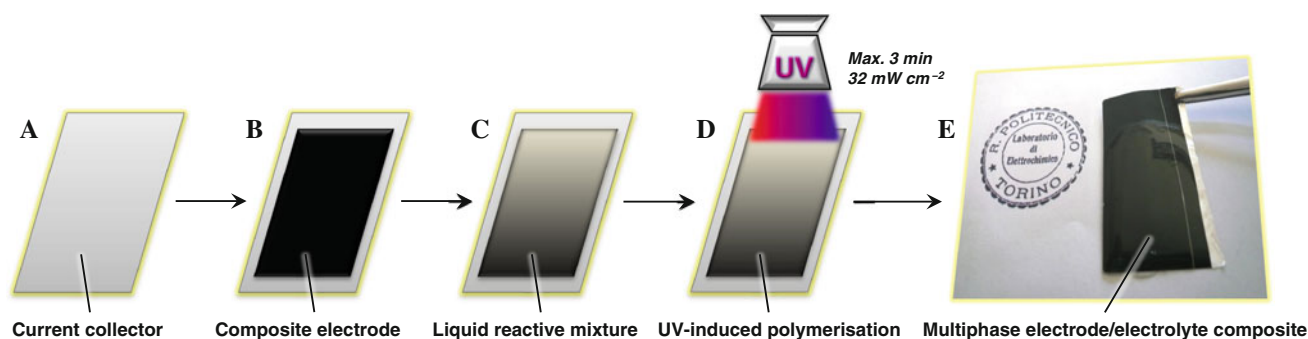


Fig. 1 Schematic representation of the multiphase electrode/electrolyte composite preparation procedure. **a** Aluminium (or copper) current collector foil. **b** Coating of the electrode paste onto the current collector. **c** After the evaporating the solvent and drying under high vacuum, the electrode layer was coated with the mixture constituting the polymer electrolyte precursor. **d** The coated sheets were covered

with UV transparent quartz boxes and this set up was later exposed to UV-irradiation for approx. 3 min under N₂ flow. **e** Photograph of a freshly prepared self-supporting multiphase electrode/electrolyte composite (final thickness ~ 150 µm) obtained by one-shot in situ photo-polymerisation technique. All the above-described procedures were carried out inside an environmentally controlled dry room

Illkirch, France) which collects the spectra in real time while the sample is irradiated by UV light, following the decrease in the allyl double bond signal at $1,636\text{ cm}^{-1}$ [15]. Thermogravimetric analyses were done in the temperature range $25\text{--}600\text{ }^{\circ}\text{C}$ using a TGA/SDTA-851 instrument (METTLER, Zurich, Switzerland) under N_2 flux at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Differential scanning calorimetry (DSC) measurements were performed from -140 to $100\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ with a DSC-30 instrument (METTLER, Zurich, Switzerland) equipped with a low temperature probe.

Morphological characterisation of the multiphase composite films was performed on freshly prepared sections of the thick films without any metallization, in order to obtain the best resolution as well as a high penetration depth. A FEI Quanta Inspect 200LV scanning electron microscope (SEM, max magnification of 1.5×10^5) equipped with an energy-dispersive X-ray analyser EDAX Genesis system with SUTW detector was employed. The samples for the cross-sectional SEM images were prepared by fracturing the given film in liquid nitrogen in order to avoid any change in the morphology.

Electrochemical impedance spectroscopy (EIS) was used to assess the ionic conductivity of the pristine polymer electrolyte membrane, while its electrochemical stability window was evaluated by running sweep voltammetry in 3-electrode test cells (model ECC-Ref, <http://elcell.com/products/test-cells/ecc-ref>, purchased from EL-Cell GmbH, Germany). A full description of these experimental procedures is reported in [13]. In order to confirm the results obtained, the tests were performed at least three times on different fresh samples. Clean electrodes and fresh samples were used for each of the above reported tests.

2.4 Assembly of the Li-based polymer cells and electrochemical tests

After UV exposure, the freshly prepared multiphase electrode/electrolyte composites were assembled and tested in laboratory-scale cells fabricated in the environmentally controlled dry room. Figure 2 illustrates the schematic cell configuration adopted for the characterisation and some examples of the lab-scale pouch cells produced.

The behaviour in lithium polymer cells of the negative and positive electrode composites was evaluated separately against a lithium metal foil counter electrode. The quasi all-solid-state test cells were fabricated by laminating a lithium foil over the multiphase composite electrode/electrolyte tape. The assemblies were housed in a coffee bag envelope (pouch cell) and, successively, sealed by hot pressing at about $100\text{ }^{\circ}\text{C}$. The electrochemical active area of the laminated cells was approx. 5 cm^2 . A laboratory-scale Li-ion polymer cell was also fabricated by contacting

the two components, i.e. the graphite composite anode/electrolyte film and the LiFePO_4 composite cathode/electrolyte film. The Li-ion polymer cell had an active material mass loading of about 4.5 mg cm^{-2} in LiFePO_4 and about 2.2 mg cm^{-2} in graphite.

The electrochemical behaviour and characteristics of the cells were investigated at ambient temperature in terms of charge/discharge cycling at different current regimes using an Arbin Instrument Testing System model BT-2000. The performance was evaluated in terms of specific capacity, charge/discharge efficiency and cycling stability. The potential cut-offs for the LiFePO_4 -based cells were fixed at 4.0 V versus Li^+/Li (charge step, lithium deinsertion) and 2.5 V versus Li^+/Li (discharge step, lithium insertion), while for the graphite-based cells at 0.02 V versus Li^+/Li (discharge step, lithium insertion) and 1.2 V versus Li^+/Li (charge step, lithium deinsertion), respectively. After a proper activation procedure [16] for both the positive and negative electrodes separately, the Li-ion polymer cell was cycled at 1C rate, referred to the cathodic mass, within $2.3\text{--}4.1\text{ V}$ versus Li^+/Li limits. Before the measurements, all the cells were kept at ambient temperature for at least 5 h to reach equilibrium.

3 Results and discussion

3.1 Characteristics of the polymer electrolyte membrane

Bisphenol A ethoxylate (15 EO/phenol) dimethacrylate is a UV-curable difunctional oligomer which can be readily polymerised to obtain a highly cross-linked membrane with a complete conversion of the methacrylic double bonds [15, 17]. The mono-functional monomer PEGMA-475 acts as a reactive diluent and it is incorporated into the network in order to reduce the cross-linking density, thus lowering the glass transition temperature (T_g) and increasing the flexibility of the overall polymer matrix. The pendant ethoxy groups ($-\text{CH}_2-\text{CH}_2-\text{O}-$) can also promote the Li^+ ion mobility. The polymer network obtained has a low T_g and, at the same time, it is highly thermally stable up to $300\text{ }^{\circ}\text{C}$. Such a highly cross-linked thermo-set polymer network can efficiently hold the liquid solvents and can also dissolve the lithium salt effectively [17, 18].

Upon exposure to UV-irradiation, the polymer electrolyte membrane obtained by copolymerising the reactive mixture containing BEMA, PEGMA-475, LiTFSI and EC-DEC (1:1 w/w) solution along with the photo-initiator was found to be transparent, self-standing, extremely flexible, non-tacky and easy to handle. It maintained optimum mechanical stability (i.e. it is flexible yet robust) and integrity after prolonged time of storage and testing.

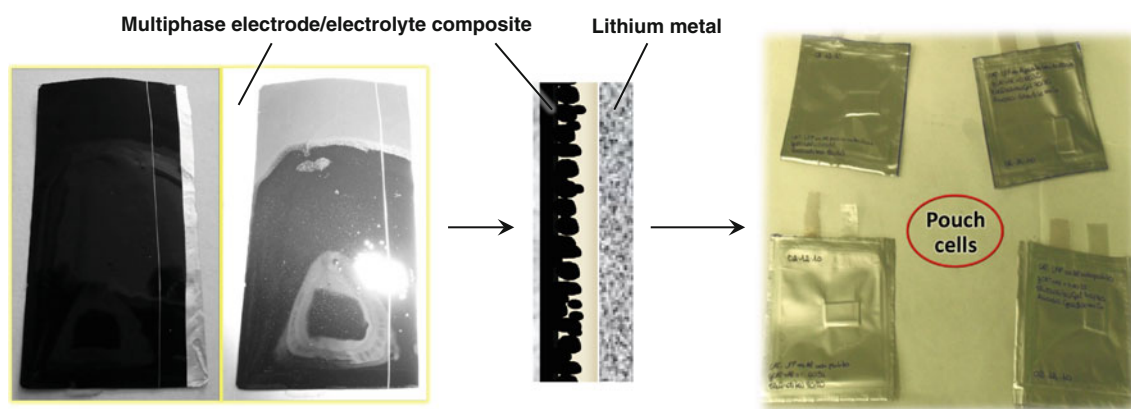


Fig. 2 Schematic representation of the assembling of the laboratory-scale “pouch cells” (multiphase electrode/electrolyte composite versus lithium metal) housed in a coffee bag envelope and used for electrochemical testing

Its most relevant chemical and structural characteristics have already been discussed (see Refs. [15, 17]), and they are summarised in Table 1.

The percentage of allyl double bond conversion during UV exposure was evaluated from kinetic studies using real-time FT-IR spectroscopy (it collects the spectra in real-time, while the sample is irradiated by UV light). The reactivity of all the monomers contained in the reactive mixture was very high in the initial stages of the UV-induced polymerisation process and the rate of polymerisation was very fast, with the quantitative yield (maximum conversion) reached in less than 120 s.

As shown in Table 1, the T_g , defined as the midpoint of the heat capacity change observed in the DSC trace during the transition from glassy to rubbery state, was found to be very low (i.e. below $-63\text{ }^{\circ}\text{C}$), indicating that at ambient temperature the polymer electrolyte membrane was in the rubbery state. Such a low glass transition temperature guarantees a high flexibility of the chain segments which will ultimately give more free path for Li^+ ions migration. The DSC trace showed only one transition in the entire temperature range considered, thus indicating that the polymer electrolyte is amorphous within a broad temperature window. Our earlier works [15, 17] showed that the thermal stability of these methacrylic-based polymeric systems is reasonably high, and the weight loss was less

than 10 wt% up to about $280\text{ }^{\circ}\text{C}$. The in situ addition of the LiTFSI-EC/DEC solution, which is incorporated into the network thus obtaining a quasi-solid polymer electrolyte, determined a lowering of the thermal stability, due to the evaporation of the organic solvent. Nevertheless, interesting T_5 and T_{10} values (i.e. the temperature corresponding to a 5 and 10 % of weight loss, respectively) were obtained, that is 139 and $181\text{ }^{\circ}\text{C}$, respectively. This result is well in the limit of applications as electrolyte for lithium battery indicating that such a polymer electrolyte membrane can be safely used in lithium polymer batteries up to around $150\text{ }^{\circ}\text{C}$, if cycled within the limits of electrochemical stability.

The ionic conductivity was monitored by EIS at variable temperatures. The corresponding values are reported in Table 1. The Arrhenius plot exhibited the VTF behaviour [13, 17] typical for amorphous materials, and the ionic conductivity was found to be dependent on the temperature. It increased more than one order of magnitude, from 1.78×10^{-4} to $3.12 \times 10^{-3}\text{ S cm}^{-1}$, when the temperature was raised to $80\text{ }^{\circ}\text{C}$ from ambient temperature. These values are reasonably high for a good performance in most standard lithium-based battery applications. The stability of the polymer electrolyte membrane versus oxidation/reduction was evaluated in terms of electrochemical stability window which was found to be as wide as

Table 1 Brief summary of the most relevant characteristics of the polymer electrolyte membrane BMPE-LiECDEC: kinetics and thermal characteristics, ionic conductivity and its stability versus storage, electrochemical stability window

Sample	Max conversion (%)	T_5/T_{10} ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)	σ at $25\text{ }^{\circ}\text{C}$ (S cm^{-1})	σ at $80\text{ }^{\circ}\text{C}$ (S cm^{-1})	Storage stability	E.S.W (V versus Li)
BMPE-LiECDEC	75 in 120 s	139/181	-63.5	1.78×10^{-4}	3.12×10^{-3}	>1 month	0–4.45

The exact weight ratio of BEMA:PEGMA:EC/DEC:LiTFSI was 35:15:35:15 with the addition of 3 wt% of photo-initiator

0.0–4.45 V versus Li, sufficient enough to a safe use in lithium-based cells with LiFePO_4 and graphite as the electrodes. The stability versus storage time was evaluated by running impedance measurements of a cell kept for long time period under open circuit conditions at ambient temperature. As already stated for similar systems [17], the polymer electrolyte membrane demonstrated to be able to retain its remarkable ionic conductivity and, thus, its integrity upon the entire storage time exceeding 1 month. Only minor fluctuations in the resistance value (correspondingly, in the ionic conductivity) with time and no deviation from linearity were found, which indicates the capability of the polymer matrix to retain the organic liquid and the salt [17]. This indirectly means that no structural or physical changes occurred in the matrix. Indeed, if there is any change in the amorphous character of the polymer matrix, this should directly affect the ionic conductivity. Such a good storage stability, in combination with the enhanced electrochemical and conductivity characteristics discussed above, good mechanical and thermal properties, are key factors in view of the practical application of the optimised composition under study in advanced Li-based batteries characterised by a long operational life.

3.2 Characterisation of the multiphase electrode/electrolyte composites by scanning electron microscopy (SEM)

Scanning electron microscopy was used to probe the morphological characteristics of the multiphase electrode/electrolyte composites. As mentioned in the experimental section, LiFePO_4 and graphite electrode materials were chosen to study the electrochemical performance of this

novel configuration. In this novel in situ UV-induced photopolymerisation procedure, pouring the polymer electrolyte precursor over the electrode film should allow the liquid precursor to penetrate into the voids of electrode particles, thus obtaining an intimate contact between the active electrode particles and the electrolyte matrix, along the whole electrode thickness. This can directly help in improving the active area at the interface between the polymer electrolyte and the electrode, correspondingly reflecting in improved specific energy and specific power of the cells. In Fig. 3, cross-sectional scanning electron micrographs, illustrating the appearance of the multiphase electrode/electrolyte composites at different degree of magnification, are shown: A(1–4) LiFePO_4 -based composite and B(1–4) graphite-based composite, respectively. Particularly at higher magnifications, it can be clearly observed that the electrolyte layer creates a conformal coating by following the contours of the electrode particles. It is seen from the cross-sectional view that the thickness of the coating is around 100 μm , but it can be easily reduced to few micrometres, thus enabling the use of this electrolyte even in microbattery systems [19, 20], where such a low thickness, compactness and good interface are fundamental.

In Fig. 4, the scanning electron micrographs at different magnifications of the as-prepared LiFePO_4 -based cathode/electrolyte assembly, clearly revealing the very good interfacial characteristics with an intimate conformal contact between the polymer matrix and the electrode film, are shown. The electrolyte deeply penetrated into the voids between the electrode material particles and conformally attached to the surface of the LiFePO_4 particles. This novel approach avoids the biggest problem of the UV cross-linked polymer electrolyte membranes which is the glassy

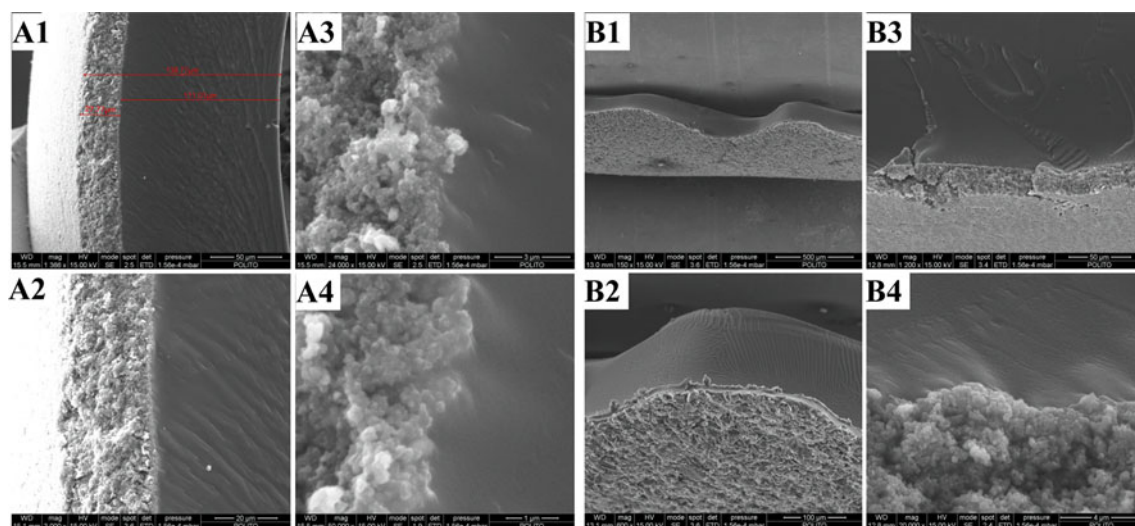


Fig. 3 Cross-sectional scanning electron micrographs illustrating the appearance of the multiphase electrode/electrolyte composites at different degree of magnification: A(1–4) LiFePO_4 -based composite and B(1–4) graphite-based composite, respectively

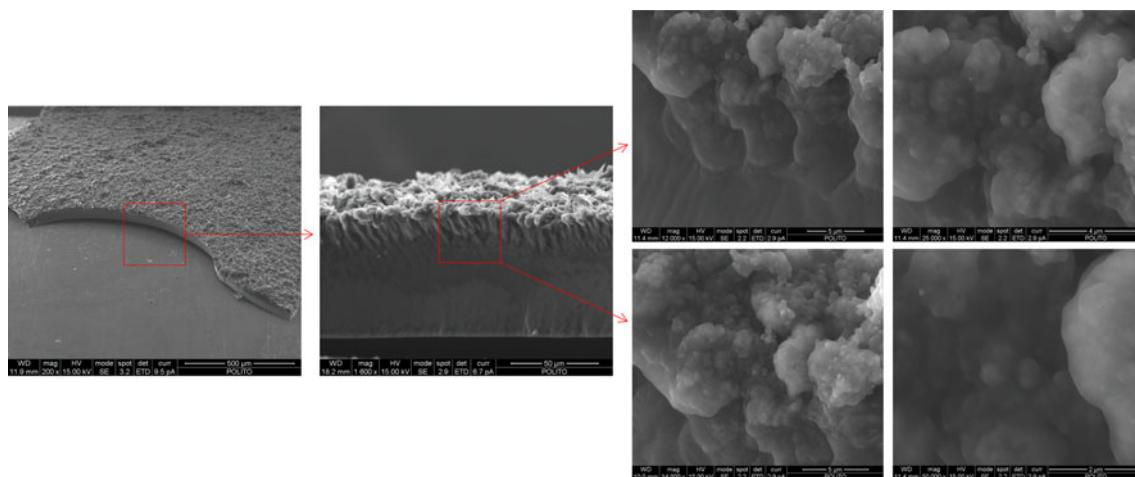


Fig. 4 Scanning electron micrographs illustrating the appearance of the LiFePO_4 /electrolyte composite at different degree of magnification. Images on the right-hand side at higher magnification clearly show the

outstanding interpenetration between the LiFePO_4 cathode particles and the polymer matrix

surface, in reality increasing the active surface area between the electrode and electrolyte interfaces. Due to this intimate contact between the electrode material grains and the polymer electrolyte matrix, the interface should not create problems arising by insufficient contact, thus enabling high electrochemical performance in lithium-based cell configuration.

Moreover, in order to test their bending endurance, the prepared multiphase electrode/electrolyte composites were rolled around cylinders of diameter ranging between 30 and 5 mm and no sign of cracking was observed.

3.3 Multiphase electrode/electrolyte testing in lithium-based polymer cells

By the optimised in situ UV-induced photo-polymerisation procedure developed, we are expecting to improve the cycling performance of the final device by an effective electrolyte–electrode interface, thus overcoming the kinetic limitations due to the ionic exchange between the electrode and the polymer electrolyte. The polymeric electrolyte surrounding the nanostructured active material particles should also act as a buffer, thus absorbing the mechanical stress associated with the insertion/extraction of Li^+ ions into/out of the active material, thus helping in maintaining the integrity and, consequently, improving the cycle life of the system.

The electrochemical behaviour in terms of charge/discharge galvanostatic cycling was tested at ambient temperature to demonstrate the feasibility of the multiphase electrode/electrolyte films to work in lithium polymer “pouch” cells, assembled as shown in Fig. 2, using lithium metal as the counter electrode. The obtained results are illustrated in Figs. 5 and 6 which show the plots of specific

capacity versus cycle number for the tested samples, along with a typical charge/discharge profile (inset). In particular, the graphite-based cell (Fig. 5) was cycled at C/10, while the LiFePO_4 -based cell (Fig. 6) was cycled at various C rates, from C/10 to 1C. As it can be observed in the insets, the charge and discharge potential profiles of the two cells are consistent with the characteristic potential trends of the standard LiFePO_4 and graphite electrodes [13, 14]. The obtained results demonstrated that, using a lithium iron phosphate electrode film intimately connected to the polymeric electrolyte, the cell can provide a very stable specific capacity exceeding 100 mAh g^{-1} even at high 1C current rate, with good Coulombic efficiency approaching 100 % (see Fig. 6). Although the specific capacity obtained is slightly lower than that obtained for the same LiFePO_4 cathode material in liquid electrolyte [14], the cycle response was also encouraging, since no decay in capacity was shown during the test. This is a convincing indication of the deep permeation of the electrode by the electrolyte and the extended interfacial contact between the electrode and the polymeric electrolyte. These effects can be ascribed to the use of the polymeric electrolyte (e.g. mechanical stress absorption, enhanced electrode/electrolyte interface and/or unwanted reaction of the polymer electrolyte with the lithium metal electrode) and the in situ polymerisation process used which allows to produce in situ the polymeric electrolyte directly onto the surface of the electrode film. Also the graphite-based electrode/electrolyte composite showed the behaviour typically expected for highly crystalline graphite materials (see Fig. 5). The initial reversible specific capacity was found to be higher than 250 mAh g^{-1} which is about 30 % lower than the theoretical limit for a graphite electrode (i.e. 372 mAh g^{-1} corresponding to the composition of the so-called “stage 1” Li-graphite

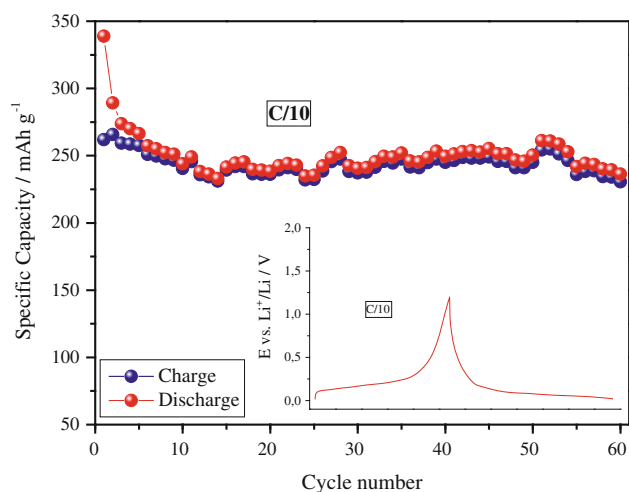


Fig. 5 Constant current charge/discharge cycling behaviour (specific capacity versus cycle number) of the lithium polymer “pouch” cell assembled by contacting the graphite-based multiphase electrode/electrolyte and a lithium metal anode, at ambient temperature and at C/10 current rate. In the *inset*, typical charge/discharge potential profiles

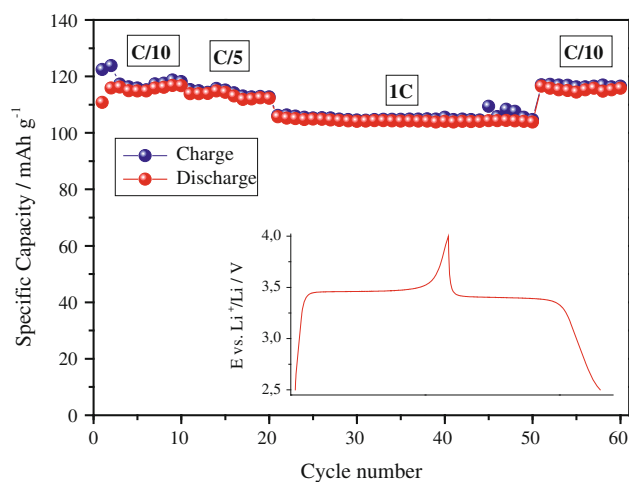


Fig. 6 Constant current charge/discharge cycling behaviour (specific capacity versus cycle number) of the lithium polymer “pouch” cell assembled by contacting the LiFePO_4 -based multiphase electrode/electrolyte and a lithium metal anode, at ambient temperature and at different current rates, ranging from C/10 to 1C. In the *inset*: typical charge/discharge potential profiles

intercalation compound, that is LiC_6). After the first cycle (SEI layer formation), the Coulombic efficiency rapidly increased to above 95 % and, subsequently, remained highly stable throughout the cycles, indicating that the formed surface film remained intact and showing good reversible cycling after the surface reactions are completed, with an average specific capacity higher than 230 mAh g^{-1} after 60 cycles.

In view of the possible practical application of these novel multiphase electrode/electrolyte composites, they were assembled in a complete Li-ion polymer battery

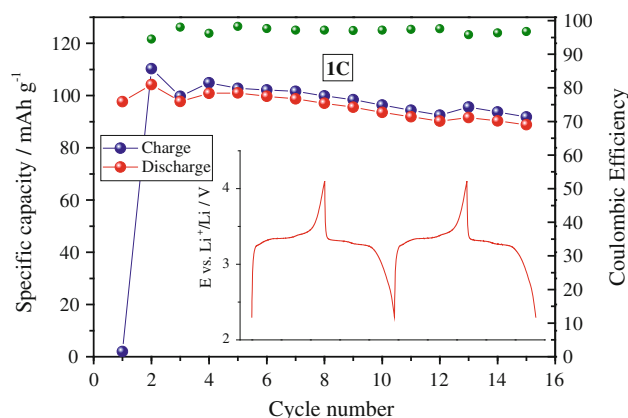


Fig. 7 Specific capacity versus cycle number profiles at 1C rate of the laboratory-scale Li-ion polymer “pouch” cell, assembled by contacting the two LiFePO_4 -based and graphite-based multiphase electrode/electrolyte composites developed. In the *inset*: typical potential versus time charge/discharge profiles. 1C = 170 mA g^{-1} is referred to the LiFePO_4 active material mass. Ambient temperature

laboratory prototype and its electrochemical behaviour was investigated by means of galvanostatic charge/discharge cycling. The assembling was done just by contacting the two composite electrode/electrolyte films and, consequently, the contact was intimate as we have used same electrolyte components; moreover, the very low T_g should help in enhancing the adhesion between them due to the similar nature and softness of the polymer matrices. The preliminary response of the prototype, assembled by contacting the LiFePO_4 -based and graphite-based composites is shown in Fig. 7. In the *inset*, some typical potential versus time profiles, obtained at ambient temperature at approx. 1C rate with respect to LiFePO_4 are shown. The maximum specific capacity obtained by the cathode/electrolyte composite developed in this work (see Fig. 6) is about half of that of the graphite-based composite (see Fig. 5), implying that the cell was cathode limited and, accordingly, its capacity was cathode rated. The obtained values between 90 and 110 mAh g^{-1} , that is very similar with respect to the maximum value obtained for the LiFePO_4 -based composite. The working potential of the Li-ion polymer cell was around 3.3 V versus Li^+/Li , reflecting the combination between the sloping profile evolving around 0.2 V versus Li^+/Li of the graphite-based composite (see the *inset* of Fig. 5) and the flat profile at about 3.5 V versus Li^+/Li of the LiFePO_4 -based one (see the *inset* of Fig. 6) [13]. The Coulombic efficiency was found to be high, exceeding 97 %, with a good cycling stability in this preliminary test. The charge–discharge performance increased with the increase in the pressure applied and also with the adhesion area of the battery. Although further efforts to reduce the cell resistance are

necessary, we successfully indicated the possibility of industrial manufacturing process of an all-solid sheet Li-ion cell.

4 Conclusions

In the present work, we demonstrated that in situ UV-induced free-radical photo-polymerisation is a suitable and versatile method for producing flexible, yet mechanically stable, high performing multiphase electrode/electrolyte composites to be used in Li-based polymer batteries. By this optimised fabrication method, methacrylic-based polymer electrolyte membranes incorporating a lithium salt and organic solvents were directly produced in a single step at the surface of standard LiFePO_4 and graphite electrode films, which could reduce the manufacturing costs and simplify the fabrication process of all-solid/quasi-solid-state thin-film-type batteries.

The characterisation and obtained results demonstrated an enhanced adhesion of the polymer electrolyte to the electrode material particles. This plays a critical role in improving the wettability and electrolyte retention, the interfacial adhesion between the electrode active material and the polymer matrix, and, correspondingly, the cycling performance at ambient temperature of the resulting lithium polymer cell assemblies. Due to the intimate contact between the electrode material grains and the polymer electrolyte matrix, the interface does not create problems arising by insufficient contact. By these novel electrode/electrolyte composites, produced by UV-induced single step photo-polymerisation process, we are able to optimise the interfacial properties between the nanostructured electrodes and the polymer electrolyte, thus they hold a great potential to be used in high-performance, versatile and cost-effective lithium-based polymer batteries.

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